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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XI. THE LOSS OF POWER COINCIDENT WITH THE ANTIKNOCK ACTION OF THE CARBONYLS OF IRON AND NICKEL IN RICH MIXTURES

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XI. THE LOSS OF POWER COINCIDENT WITH THE ANTIKNOCK ACTION OF THE CARBONYLS OF IRON AND NICKEL IN RICH MIXTURES[1]

By R. O. King[2] and Edwin J. Durand[3]

Abstract

Experiments are described which show that the increase in usable compression ratio obtained on adding iron or nickel carbonyl to rich mixtures with air, of hydrocarbon fuel used in the high temperature conditions of the A.S.T.M.–C.F.R. motor method of knock testing, is not accompanied by a commensurate increase in power. The percentage by which the observed power for the doped fuel is less than that obtainable if a nonknocking fuel were used at the same compression ratio has been determined for various additions of the iron and nickel carbonyls of Fuel *S*, a commercial gasoline. The loss of possible power when using iron carbonyl in the concentration of 0.50 cc. per liter, increased from 2% at maximum power mixture strength to over 22% at extremely rich mixtures. The loss is attributed to appreciable oxidation of the fuel to final products, prior to the completion of compression, especially when doped fuel is used. Thus the experimental results confirm the theory, advanced in Part III, that metallic antiknocks act by promoting the high temperature surface (heterogeneous) oxidation of hydrocarbon fuel to steam and carbon dioxide; not by inhibiting a homogeneous oxidation reaction by the breaking of reaction chains, as generally supposed.

Introduction

The theories that organic peroxides cause detonation and that the antiknock organometallic compounds act by destroying the peroxides or preventing their formation were first advanced by Callendar and associates (2, 3). The theories in one form or another are still current. Egerton and Gates (5) regard antiknocks "as negative catalysts which react with and remove those substances (peroxides) which auto-catalyse combustion". Egerton in a later publication (4) assumes that preflame oxidation in the engine is a homogeneous reaction, that it proceeds to ignition in the end gas by chain reactions, and that the metallic antiknocks act by breaking the chains. Ubbelohde (15, p. 2943) refers to "the complete inhibition of all oxidation by the addition of antiknocks". Prettre (12, p. 2956) concludes that "the influence of antiknocks in engines can only be explained by their inhibitory action on thermal combustion". Beatty and Edgar (1, p. 2934 and p. 2936) consider that "there is little evidence for the occurrence of significant surface reactions in an engine" and conclude that "antiknock agents act as inhibitors for the slow oxidation in the end gas. Their

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effect is to break short the reaction chains and so prevent the chain development from reaching that critical point at which its multiplication begins".

The current theory mentioned above is no longer tenable in view of the experiments described in Parts I (6), II (7), and III (8). They show that the products of *surface oxidation* of engine fuel at *high temperatures* delay the onset of detonation or knocking combustion. The products are steam, carbon dioxide, and carbon monoxide when undoped fuels are used but when the fuel contains metallic dope the products tend to be steam and carbon dioxide only, at any temperature, and the antiknock effect is enhanced accordingly.

The difference between rates of surface oxidation of doped and undoped fuel at high temperatures and the effect of mixture strength on reaction rates were shown by experiments made when using reaction chamber No. 10 and are described in Part VII (10). Rates of reaction were found to increase by 100% on raising the temperature from 600° to 650°C. and to increase by 100% at any temperature within the range, on increasing mixture strength from 25% weak to 100% rich. Nearly 20% of the oxygen in the weak pentane–air mixture passing through the chamber was reacted at 600°C., and 80% of the oxygen in a 100% rich mixture was reacted at 650°C. Similar rates of reaction but at *temperatures 150°C. lower* were obtained when iron carbonyl was added to the pentane.

Temperatures attained by the end gas in an engine when combustion is 90% complete are estimated to be somewhat greater than 650°C. even at the low compression ratio of 4.0 (9, p. 233), and during the whole of the combustion period the "skin" surface temperatures which determine the velocity of surface oxidation would be higher to an unknown degree, because of radiation from the flame. Surface oxidation prior to completion of compression would result in a loss of power. The greater loss would occur if oxidation were promoted to final products by the use of metallic antiknocks, especially as reaction would then proceed at high velocity even at temperatures as low as 430°C. (9, p. 438).

Thus the experiments described in this Part show the *difference* in the effects on power and knock, due to surface oxidation, as between Fuel *S* and the same fuel containing iron or nickel antiknocks.

Section 1

Experimental Arrangements and Results

The C.F.R. knock testing engine used for the experiments was "standard" except that arrangements were made for accurate measurement of power output.

The belt driven main and auxiliary generators of the C.F.R. unit were disconnected from the engine. The main generator was then driven as a motor from the laboratory d-c. supply and it in turn drove the auxiliary generator which supplies current for the engine auxiliaries, such as the bouncing pin, the

oil heater, the intake air heater when used, and the ignition system. The engine was then direct connected to a d-c. swinging field dynamometer with beam type scale. Thus, net brake horsepower was measured. Indicated horsepower was obtained by adding, to the B.H.P. observed when the engine was developing power, the brake horsepower required to overcome friction and pumping losses when fuel was not added to the air supply and the engine was "motored" by the dynamometer. "Motoring" loss was measured after every set of power observations as soon as possible after stopping the fuel supply.

All the experiments to be discussed were made in the conditions of the C.F.R.–A.S.T.M. motor method of knock testing; mixture temperature, 300°F.; jacket coolant temperature, 212°F.; and engine speed, 900 r.p.m.

Fuel *S*, Lot 2, a commercial grade of gasoline, generally similar to Fuel *S*, Lot 1 (11, pp. 212-213), was used for the experiments.

The experimental results are given by the graphs of Figs. 1 to 5. A uniform system of lettering is used. Thus variation of the compression ratio for standard knock intensity with increase of mixture strength is shown for the doped fuel by the A graphs and for the undoped fuel by the A_1 graphs. The variation of indicated horsepower (I.H.P.) with increase of mixture strength is shown for the doped fuel by the B graphs and for the undoped fuel by the B_1 graphs.

The term "usable C.R." will be used hereafter as an abbreviation of "compression ratio for standard knock intensity", as defined in Part VIII (9, p. 215).

It is shown by the A_1 graphs that the minimum value of the usable C.R. was obtained when the rate of fuel consumption of the undoped fuel was 1.85 lb. per hr., and, as explained in Part IX, it may be assumed that the fuel–air mixture was then approximately "correct" and consequently that percentages by which the mixture strength is rich or weak can be calculated accordingly for other rates of fuel consumption.

Nickel Carbonyl Additions to Fuel *S*

Concentration: 0.25 cc. per Liter of Nickel Carbonyl. Fig. 1

The graphs of Fig. 1 show that nickel carbonyl in the concentration in the fuel of 0.25 cc. per liter is of slight effect to increase the usable C.R. at correct mixture strength and that there is no increase of power.

Maximum power is obtained at a rate of fuel supply of 2.3 lb. per hr., that is, with a mixture strength 24% rich. The value 4.02 I.H.P. is the same for both fuels within the accuracy of measurement, although the usable C.R. for the doped fuel was 6.5 and for the undoped fuel 6.07. That is, an increase of 0.43 in usable C.R. obtained on adding the nickel carbonyl was not accompanied by any increase of power.

It will be noted that for rates of fuel consumption exceeding 2.5 lb. per hr. the large increases in usable C.R. obtained accordingly were accompanied by relatively large *decreases* in power.

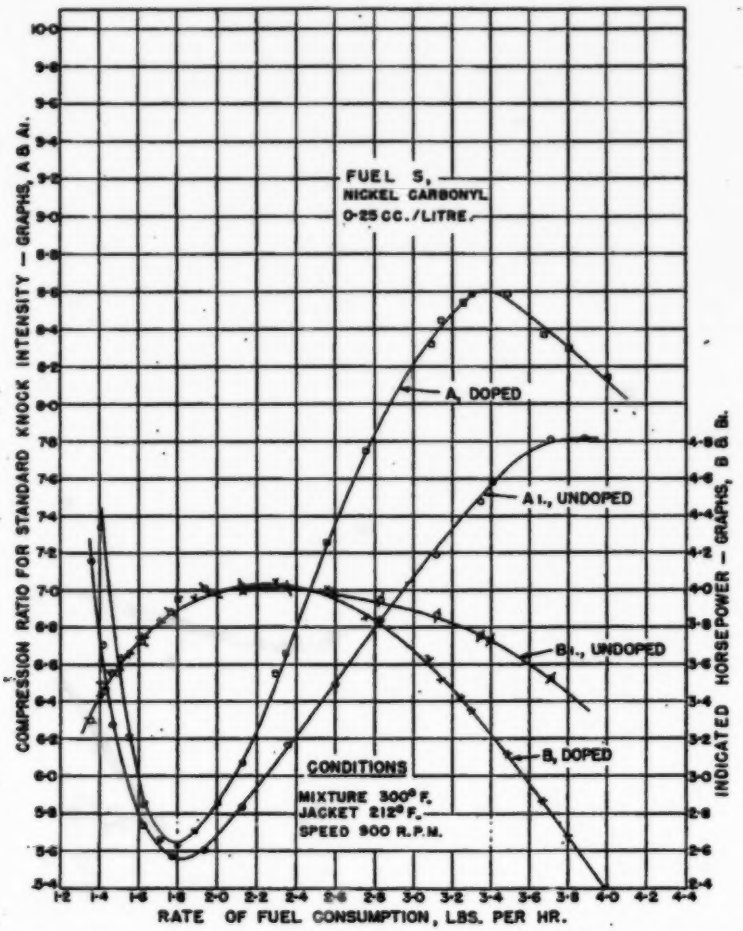

FIG. 1. *The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 0.25 cc. per liter.*

Concentration: 0.50 cc. per Liter of Nickel Carbonyl. Fig. 2

The effects on power and usable C.R. are shown in the graphs of Fig. 2. At the maximum power mixture strength, 2.3 lb. of fuel per hr., an increase of from 4.02 to 4.18 I.H.P. is obtained for a usable C.R. increase of from 6.07 to 6.80. The beneficial effect on power diminishes with further increase in mixture strength although usable C.R. increases rapidly, and when rate of fuel

consumption reaches 2.9. lb. per hr. the power developed by the doped mixture at a usable C.R. of 8.34 is the same as that for the undoped fuel at a usable C.R. of 6.92. The mixture strength being still further increased, usable C.R. increases accordingly but the power becomes *less* than for the undoped fuel at very much lower usable compression ratios.

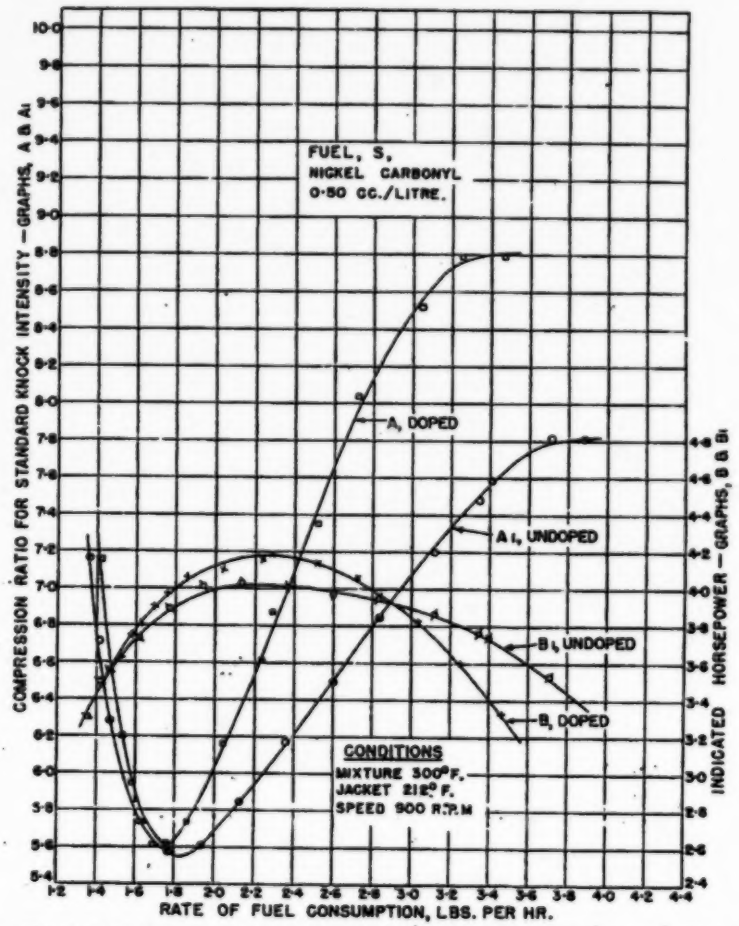

FIG. 2. *The relation between usable compression ratio and power as affected by nickel carbony in the fuel in the concentration of 0.50 cc. per liter.*

Concentration: 1.0 cc. per Liter of Nickel Carbonyl. Fig. 3

The effects on power and usable C.R. are shown by the Graphs of Fig. 3. At the maximum power mixture strength, 2.3 lb. of fuel per hour, I.H.P. increases from 4.02 to 4.34 for the very large increase in usable C.R. of from 6.07 to 7.85.

A usable C.R. of 10, the limiting value for the engine as used, was attained for the doped fuel on increasing the rate of fuel consumption to 2.9 lb. per hr. The increase in usable C.R. from the 6.92 of the undoped fuel was accompanied by an increase of from 3.92 to 4.15 I.H.P., that is, less than 6%.

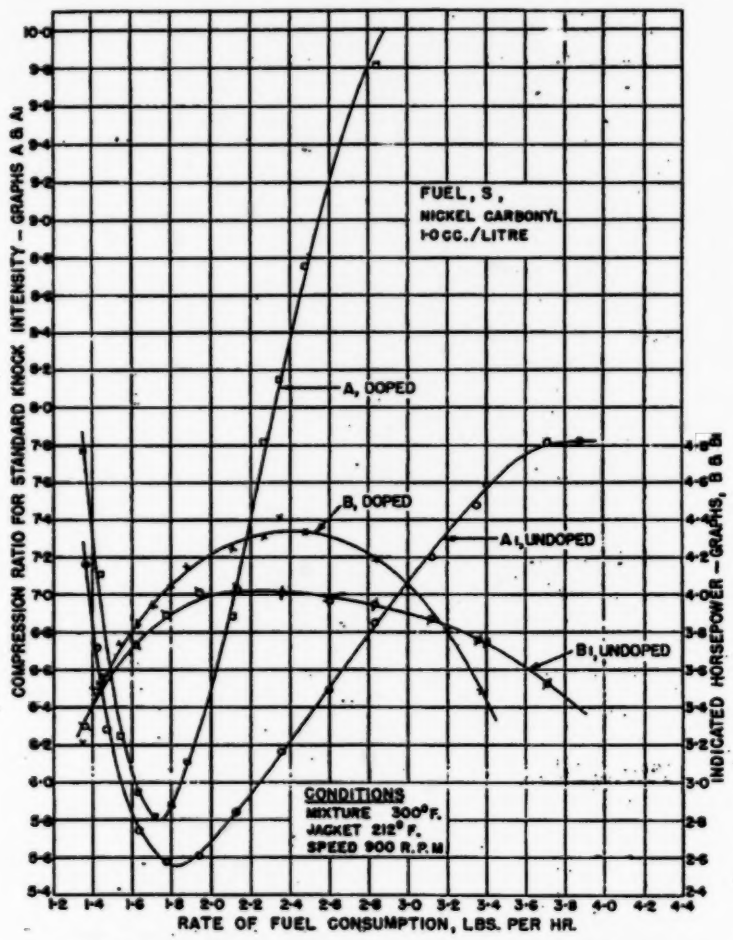

FIG. 3. *The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 1.0 cc. per liter.*

Equal power was developed by the doped and undoped fuels at a fuel consumption of 3.17 lb. per hr. The usable C.R. for the undoped fuel was then 7.25 but that for the doped fuel was greater than 10.

IRON CARBONYL ADDITIONS TO FUEL *S*

Concentration: 0.25 cc. per Liter of Iron Carbonyl. Fig. 4

The effects on power and usable C.R. are shown by the graphs of Fig. 4. The antiknock effect of the iron in respect of weak mixtures is noteworthy. Thus the minimum value of the usable C.R. 5.68 was observed when the rate

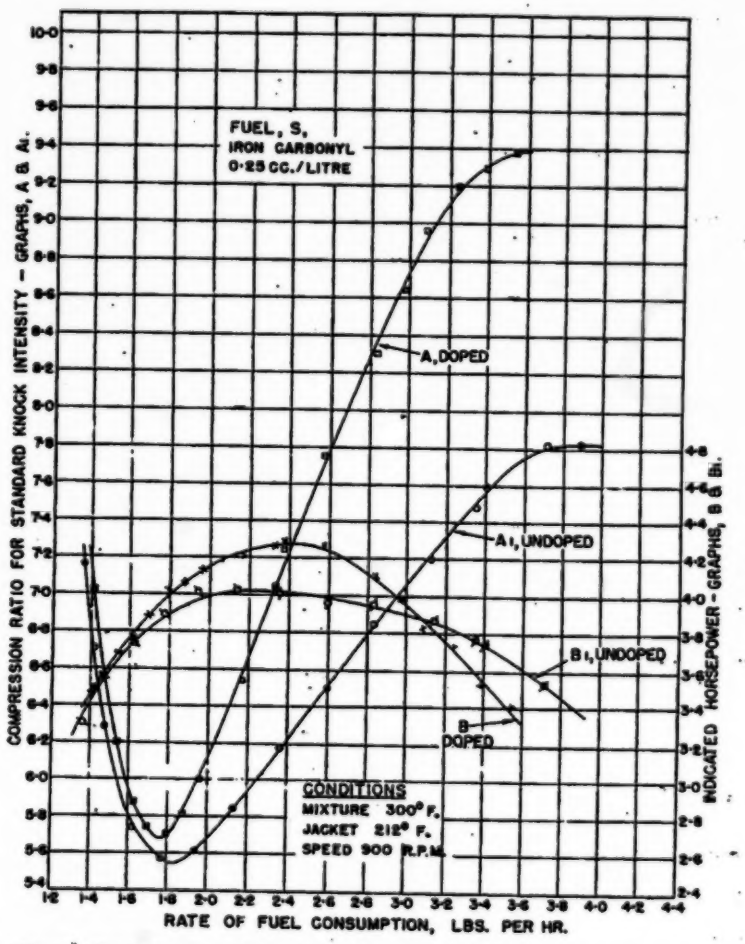

FIG. 4. *The relation between usable compression ratio and power as affected by iron carbonyl in the fuel in the concentration of 0.25 cc. per liter.*

of doped fuel consumption was 1.76 lb. per hr., whereas when Fuel *S* was used undoped, the minimum usable C.R. was 5.54, observed for a rate of fuel consumption of 1.85 lb. per hr. The I.H.P. for the undoped fuel used at 1.85 lb. per hr. was 3.93 and for the doped fuel 4.04 at the same rate of fuel consump-

tion, that is, a power increase of 2.8% was obtained on increasing the usable C.R. from 5.54 to 5.78.

The maximum I.H.P. of 4.28 was obtained for the doped fuel when the rate of fuel consumption was 2.4 lb. per hr.; the usable C.R. being then 7.28. The I.H.P. for the undoped fuel at the same rate of consumption was 4.0; the usable C.R. being then 6.21; that is, a power increase of 7% was obtained on increasing the compression ratio from 6.21 to 7.28.

The same I.H.P., namely 3.9, was obtained for both fuels when the rate of consumption was 3.1 lb. per hr. although the usable C.R. for the doped fuel was 8.95 as compared with 7.2 for the undoped fuel.

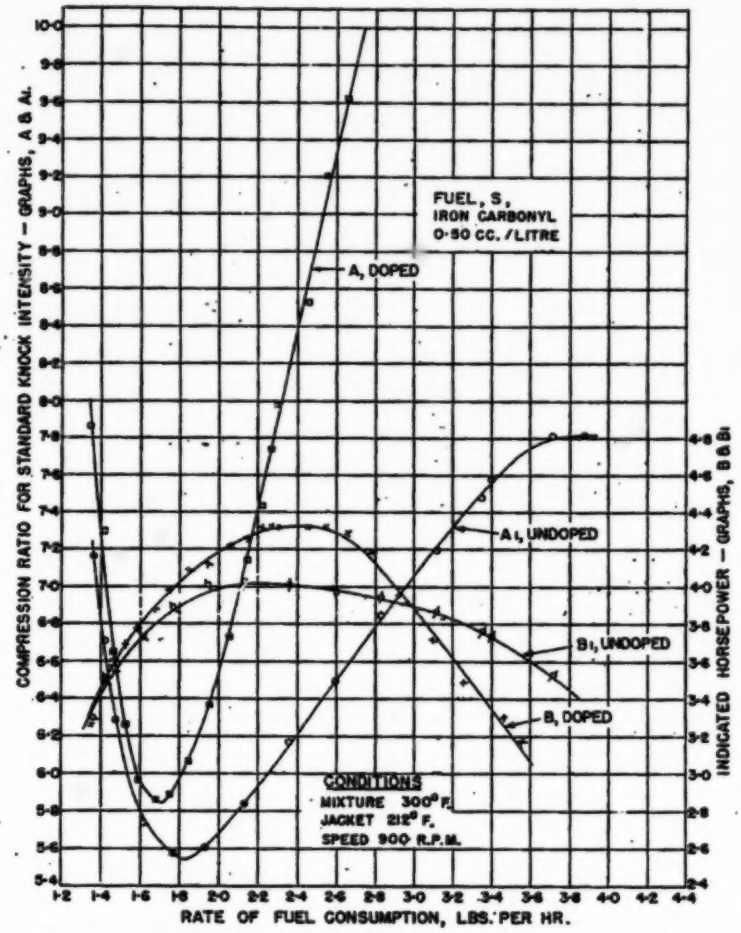

FIG. 5. *The relation between usable compression ratio and power as affected by iron carbonyl in the fuel in the concentration of 0.50 cc. per liter.*

Concentration: 0.50 cc. per Liter of Iron Carbonyl. Fig. 5

Considering a rate of fuel supply of 1.85 lb. per hr., usable C.R. increased from 5.54 to 6.07 and I.H.P. from 3.93 to 4.07, that is 3.6% on adding the carbonyl.

The maximum I.H.P. of 4.32 for the doped fuel was obtained for a rate of consumption of 2.4 lb. per hr.; the usable C.R. then being 8.4. The I.H.P. for the undoped fuel at the same rate of consumption was 4.0 and the usable compression ratio 6.21. That is, a power increase of 8% only was obtained on increasing the compression ratio from 6.21 to 8.4.

The same I.H.P., namely 3.9, was obtained for both fuels when the rate of consumption was 3.0 lb. per hr. The usable compression ratio for the undoped fuel was then 7.06, while the doped fuel was used at a compression ratio of 10, which is lower than the *usable value which could not be determined* because it exceeded the measurement limit.

Section 2

Discussion of the Experimental Results

Little if any adverse effect on power would occur if the temperature required for appreciable surface oxidation were attained late in the combustion period, which generally extends beyond top dead center. The required temperature would not, for example, be expected during compression in an unsupercharged engine at moderate compression ratios with the ingoing mixture raised in temperature solely by the usual induction pipe heating.

It has, however, been shown by laboratory experiments mentioned earlier that a fuel such as pentane doped with iron carbonyl and in rich mixtures with air is oxidized to steam and carbon dioxide with high velocity on surfaces at temperatures as low as 430°C. Higher temperatures would be expected during compression, on surfaces in the cylinders of supercharged aircraft engines, and the experimental results of Section (1) support the view that, even in the C.F.R. engine run in A.S.T.M. knock testing conditions, surface temperatures are high enough to cause preflame oxidation sufficient for an easily measurable adverse effect on power, when rich mixtures containing iron or nickel carbonyl are used.

The adverse effect on power, coincident with the antiknock effect of the metallic dopes in rich mixtures used in the C.F.R. engine, has been calculated from the experimental results of Section (1), see Tables I, II, and III below. The calculations require data for the possible percentage increase in power with increase in compression ratio for a nonknocking fuel used at compression ratios extending to 10. The data given by the graph of Fig. 6 are from those compiled by Pye (14, p. 49) for compression ratios of from 4 to 8, and have been extrapolated to a compression ratio of 10. The assumption is made that percentage increase of power with increase of compression ratio as given by the graph of Fig. 6 can be applied generally.

TABLE I

FUEL *S* PLUS 0.50 CC. IRON CARBONYL PER LITER

Rate of fuel consumption, lb./hr.	Mixture, per cent rich	Increase of usable C.R.	Observed change of I.H.P.	Percentage increase of I.H.P.	Possible % increase of I.H.P.
2.10	18.8	5.8 to 6.95	4.02 to 4.25	5.72	7.93
2.30	24.3	6.07 to 7.9	4.02 to 4.31	7.2	11.8
2.50	35.0	6.36 to 8.85	4.00 to 4.32	8.0	14.2
2.70	46.0	6.65 to 9.8	3.96 to 4.23	6.8	17.5
3.00	62.0	7.07 to +10	3.90 to 3.90	0.0	15.2+
3.40	84.0	7.57 to +10	3.73 to 3.34	−10.5	12.3+

TABLE II

FUEL *S* PLUS 0.50 CC. NICKEL CARBONYL PER LITER

Rate of fuel consumption, lb./hr.	Mixture, per cent rich	Increase of usable C.R.	Observed change of I.H.P.	Percentage increase of I.H.P.	Possible % increase of I.H.P.
2.10	18.8	5.81 to 6.27	4.02 to 4.16	3.5	3.5
2.30	24.3	6.07 to 6.81	4.02 to 4.18	3.97	4.73
2.50	35.0	6.35 to 7.37	4.00 to 4.13	3.25	6.63
2.70	46.0	6.65 to 7.90	3.96 to 4.05	2.27	7.87
3.00	62.0	7.07 to 8.50	3.90 to 3.84	−1.54	8.23
3.40	84.0	7.57 to 8.80	3.73 to 3.41	−8.6	6.15

TABLE III

FUEL *S* PLUS 1.0 CC. NICKEL CARBONYL PER LITER

Rate of fuel consumption, lb./hr.	Mixture, per cent rich	Increase of usable C.R.	Observed change of I.H.P.	Percentage increase of I.H.P.	Possible % increase of I.H.P.
2.10	18.8	5.81 to 6.9	4.02 to 4.27	6.2	6.9
2.30	24.3	6.07 to 7.86	4.02 to 4.33	7.7	11.5
2.50	35.0	6.35 to 8.8	4.00 to 4.34	9.2	14.5
2.70	46.0	6.65 to 9.55	3.96 to 4.27	7.8	16.4
3.00	62.0	7.07 to +10	3.90 to 4.05	3.9	15.2+
3.40	84.0	7.57 to +10	3.73 to 3.43	−8.0	12.3+

Thus, with reference to Table I, for example, maximum power, 4.02 I.H.P., was obtained over the range of mixture strength, 18.8 to 24.3% rich. On adding iron carbonyl in the concentration of 0.50 cc. per liter to the richer mixture, usable C.R. could be raised from 6.07 to 7.9. The corresponding increase in

I.H.P. taken from the experimental results, Fig. 5, was 7.2%. If, however, the fuel had been a nonknocking variety, the increasing of the compression ratio from 6.07 to 7.9 would have resulted in an increase of 11.8% in I.H.P. according to the data of Fig. 6. That is, attainment of the higher usable compression ratio by the use of metallic antiknock was accompanied by a loss of 4.6% of the possible increase in I.H.P.

The power obtainable when using rich mixtures of *undoped* fuel may be affected adversely by the enhanced tendency of such mixtures to oxidize on surfaces in the combustion space of the C.F.R. engine when operated in the high temperature conditions of the A.S.T.M. knock testing method. There-

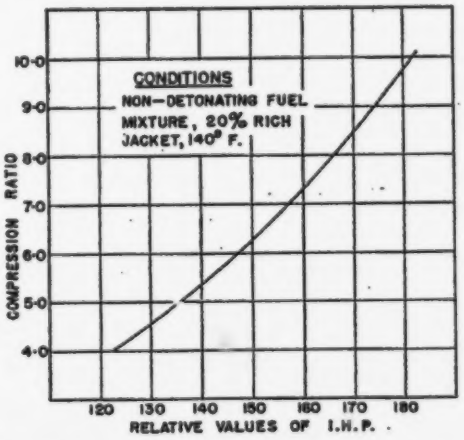

FIG. 6. *The relation between compression ratio and power for a nonknocking fuel used in the Ricardo E 35 engine.*

fore, the experimental results given in this paper are regarded as representing differences in the adverse effect on power of surface oxidation, between Fuel *S* and the same fuel containing iron or nickel antiknock.

Mixture strengths given in the tables range from 18.8 to 84% rich. The maximum I.H.P., Fuel *S*, was constant within the accuracy of measurement over the mixture range 19 to 35% rich and at 84% rich it was 6% only, less than at 2.8% rich. When an engine is run with the compression ratio fixed, it is usually found that power reaches a maximum within the mixture range 10 to 20% rich and diminishes slowly with further increase (13, p. 134). It is to be noted accordingly that values of I.H.P. given in the tables were obtained on increasing compression ratio with increase of mixture strength to maintain a standard knock intensity.

The loss of possible I.H.P. coincident with the antiknock action of the iron and nickel carbonyls is shown by differences between the percentages of Columns 5 and 6 of the tables.

It will be noted by reference to Tables I and II that iron carbonyl in the concentration of 0.50 cc. per liter possesses nearly the same antiknock effect as nickel carbonyl in double the concentration. It will suffice, therefore, to mention the principal features of the experimental results obtained when using iron carbonyl.

The possible loss of power coincident with the antiknock action of iron carbonyl in the concentration of 0.50 cc. per liter, Table I, extends from 2 to nearly 11% as mixture strength is increased from 19% to 46% rich. The loss at 62% rich was greater than 15% and at 84% rich it was greater than 22%. The full extent of the losses at mixture strength greater than 46% rich could not be measured because the compression ratio was then off the scale of the engine when the doped fuel was used.

Concluding Comment

The principal interest of the experimental results lies in their confirmation of the theory, advanced in Part III (8), that the metallic antiknocks act by *promoting* the high temperature surface oxidation of hydrocarbon fuel to steam and carbon dioxide, not by inhibiting a homogeneous oxidation reaction by breaking reaction chains.

Acknowledgments

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